ULTRA-HIGH PRECISION Sr ISOTOPE MEASUREMENTS: APPLICATIONS TO EARLY SOLAR SYSTEM ISOTOPIC HETEROGENEITY AND CHRONOLOGY. Y. Ku[1] and S. B. Jacobsen[1], [1]Department of Earth and Planetary Sciences, Harvard University. 20 Oxford Street, Cambridge, MA02138, USA. (yku@g.harvard.edu)

Introduction: Among the four stable isotopes of Sr (^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr), only ^{87}Sr varies due to ingrowth from the radioactive decay of ^{87}Rb providing an important early solar system chronometer for processes that fractionate Rb from Sr [1]. In particular, the ^{87}Rb-^{87}Sr chronometer is an important tool in dating the volatile element depletion of rocky early solar system materials [2,3]. Relatively large ^{84}Sr isotope anomalies were found in two Allende Ca-Al-rich inclusions (EK1-4-1and C1) [4]. Over the last decade a number of papers have also reported measurable ^{84}Sr anomalies in bulk meteorites [5-11]. The use of initial ^{87}Sr/^{86}Sr as a chronometer for the early solar system requires careful evaluation of such anomalies, but the available data on ^{84}Sr/^{86}Sr variations exhibit many inconsistencies due to the difficulty of ^{84}Sr/^{86}Sr measurements.

A detection of an anomaly in ^{84}Sr/^{86}Sr requires precise measurement of ^{84}Sr, which is only 0.56% of the total solar system Sr. Therefore, measurements of bulk meteorites are very difficult considering the small range of variations in this ratio (100-200 ppm). Even the most recent reports on TIMS data for ^{84}Sr/^{86}Sr [6,12-13] have substantial uncertainties, up to 50 ppm.

The newly developed ATONA amplification technology from Isotopx has eliminated the need for a "feedback resistor" [14], making it very promising for applications to measurements of small isotopes (such as ^{84}Sr) relative to large isotopes (in this case ^{86}Sr and ^{88}Sr). This is because ATONA provides a substantial reduction in amplifier noise, as well as a dramatic increase in dynamic range. Analysis can be performed for signals ranging from 10's cps up to 1nA (equivalent to 100V on 10^{11} ohm resistor amplifier).

We report our initial data on ^{87}Sr/^{86}Sr and ^{84}Sr/^{86}Sr for both terrestrial and extraterrestrial samples. So far we analyzed one terrestrial basalt standard, BHVO-2, the standard NIST SRM-987, one carbonaceous chondrite (Allende), one ordinary chondrite (Bruderheim), and two achondrites, a Martian meteorite (Nakhla) and a eucrite (Juvinas). The Allende (CV3) and Bruderheim (L6) samples are aliquots of homogeneous and representative rock powders of 34 grams and 200 grams, respectively. Samples containing ~ 2μg of Sr, were dissolved and repeatedly heated in a mixture of HF, HNO_3, and HCl in the latest *iWave* system of *Mars* 6 Microwave. Solutions were re-dissolved in 0.5 mL 8N HNO_3 and loaded on the preconditioned columns of 20 μg Eichrom Sr resin (equals to 0.5 ml slurry in MQ H_2O). After loading the samples, 5.5 mL 8N HNO_3 was eluted, and 5 mL Sr was collected in MQ H_2O.

Mass spectrometry methods and results: Sr isotope measurements were made with a new Isotopx Phoenix TIMS with ATONA amplifiers. Samples of 0.5μg to 1μg of Sr were loaded on single Re filaments with a Ta_2O_5 activator, and were measured with a filament current of ~ 3.2-3.6 A. Extensive testing of various loading and running techniques was carried out in this initial work. To make an effective use of the ATONA amplifiers, it is important to have a strong ^{84}Sr signal. We initially aimed for ^{84}Sr signal slightly above 100 mV, corresponding to a ^{88}Sr signal of ~15 V. The ^{88}Sr ion beam intensities obtained for our samples and standards are shown as a function of the measurement cycles in Fig.1. Each cycle represents a static 10-second measurement of all Sr isotopes. We found that most samples could be run with a 20 V signal for ^{88}Sr, and our best loading result (Juvinas) produced a continuing 70-90 V signal for ^{88}Sr over 400 cycles.

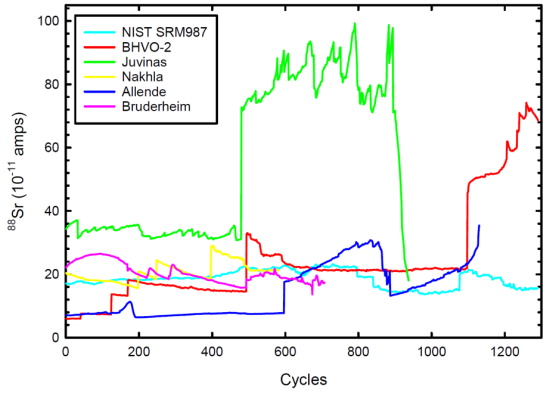

Figure 1. ^{88}Sr ion beam intensities for samples measured using a Isotopx Phoenix TIMS with ATONA.

The measurements were corrected for fractionation with the exponential law to a value of 0.1194 for ^{86}Sr/^{88}Sr. Grand mean precisions (1 sigma) for ^{87}Sr/^{86}Sr and ^{84}Sr/^{86}Sr after correcting for fractionation are shown as a function of number of cycles in Fig. 2. The curves are based on the measured standard deviations of these ratios for each sample. The 1 σ uncertainties better than 5 ppm and 1 ppm for ^{87}Sr/^{86}Sr can be achieved in 100 and 2000 cycles, respectively. We can get the ^{84}Sr/^{86}Sr precision better

than 20 ppm in 100 cycles and better than 3 ppm in 2000 cycles.

Fractionation corrected $^{84}Sr/^{86}Sr$ and raw $^{88}Sr/^{86}Sr$ ratios for 100 cycle blocks for each sample are shown in Fig. 3. In particular, the NIST SRM-987 and USGS BHVO-2 standards show a wide range of average mass dependent fractionation ($^{88}Sr/^{86}Sr$-raw) between blocks of data, but no obvious major effects on the results of $^{84}Sr/^{86}Sr$. This indicates that the potential problems of correcting fractionation in our measurements using an exponential law are negligible. An analogous plot for $^{87}Sr/^{86}Sr$ yielded the same result.

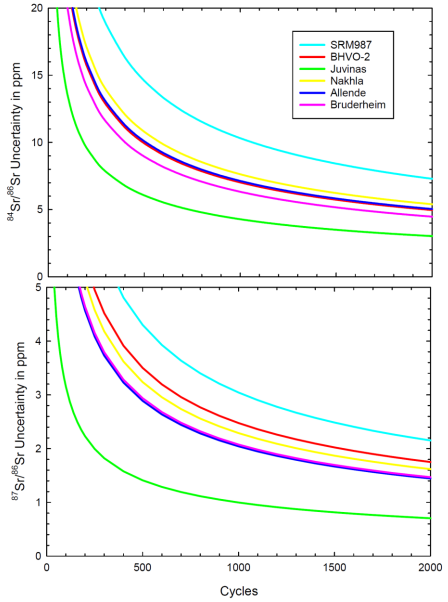

Figure 2. Uncertainties in $^{84}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ as a function of measured cycles.

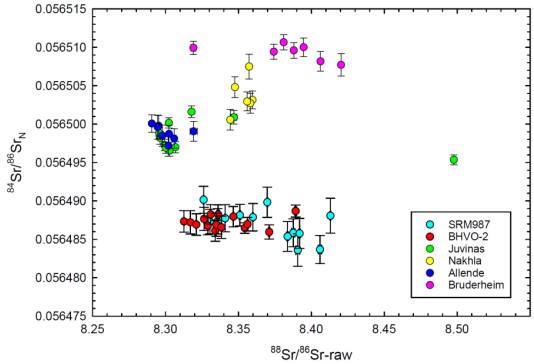

Figure 3. Block data (100 cycles in each block) for each samples (1 sigma error bars).

The NIST SRM-987 standard was analyzed and yielded values of $^{87}Sr/^{86}Sr = 0.710252\pm2$ and $^{84}Sr/^{86}Sr = 0.0564870\pm5$, and BHVO-2 yielded values of $^{87}Sr/^{86}Sr = 0.703467\pm5$ and $^{84}Sr/^{86}Sr = 0.0564872\pm3$. For the Juvinas eucrite, we obtained a very precise ratio of $^{87}Sr/^{86}Sr = 0.6998075\pm5$ in 900 cycles. According to the age of 4.561 Ga [15], and the $^{87}Rb/^{86}Sr$ ratio of 0.0117 in this sample, we obtained an initial $^{87}Sr/^{86}Sr$ of 0.6990417 ± 5. This value agrees with the previous published initial $^{87}Sr/^{86}Sr$ of basaltic eucrites (BABI) of 0.69905 ± 1 [16], after correcting for the different values measured in seawater Sr.

Discussion and conclusions: Fig. 4 shows the grand mean values of fractionation corrected $^{84}Sr/^{86}Sr$ and raw $^{88}Sr/^{86}Sr$ ratios in the samples and standards. Unexpectedly, the meteorites plot along a linear trend while two terrestrial standards are on a different horizontal trend. More measurements are needed to confirm if this pattern extends to more extraterrestrial samples or is an artifact of small sample sets. We conclude that the new ATONA technology can be used to determine $^{87}Sr/^{86}Sr$ ratio to better than 1 ppm, and $^{84}Sr/^{86}Sr$ ratio to better than 5 ppm. This can be done effectively with an ionization technique that allows ^{88}Sr ion beam intensities to be close to the limit of the ATONA amplifiers of 100 Volts (10^{-9} amps). These initial results suggests it may be possible to obtain a clear resolution of what initial $^{87}Sr/^{86}Sr$ variations are due to volatility, and what are due to initial solar system isotopic heterogeneity.

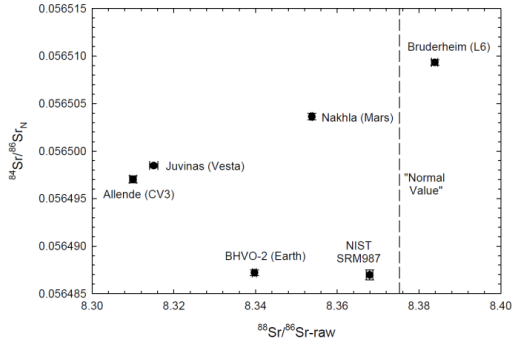

Figure 4. Grand mean values of $^{84}Sr/^{86}Sr$ ratio for each sample studied after correcting for fractionation.

References: [1] Papanastassiou D. A. and Wasserburg G. J. (1969) *EPSL,* 5, 361–376. [2] Gray C. M., Papanastassiou D. A. and Wasserburg G. J. (1973) *Icarus*, 20, 213–239. [3] Halliday A. N. and Porcelli D. (2001) *EPSL,* 192, 545–559. [4] Papanastassiou D. A. and Wasserburg G. J. (1978) *GRL*, 5, 595–598. [5] Andreasen R. and Sharma M. (2007) *APJ,* 665, 874–883. [6] Charlier B.L.A. et al. (2019) *GCA*, 265, 413–430. [7] Hans U. et al. (2013) *EPSL,* 374, 204–214. [8] Moynier F. et al. (2010) *EPSL*, 300, 359–366. [9] Moynier F. et al. (2012) *APJ,* 758, 45. [10] Paton C. et al. (2013) *APJL*, 763, L40. [11] Yokoyama T. et al. (2015) *EPSL*, 416, 46–55. [12] Henshall T. et al. (2018) *Chem. Geol*., 482, 113–120. [13] Yobregat E. et al. (2017) *J. Anal. At. Spectrom*., 32, 1388–1399. [14] Yardley S. et al. (2018) *Isotopx*, Technical Note T30182. [15] Hopkins M.D. et al. (2015) *Icarus*, 245, 367-378. [16] Wasserburg G. J. et al. (1977) *EPSL*, 35, 294-316.